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A SHOCK TUBE STUDY OF THE IGNITION DELAY OF HYDROGEN-AIR MIXTURES NEAR THE SECOND EXPLOSION LIMIT

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AIR FORCE AERO PROPULSION LABORATORY
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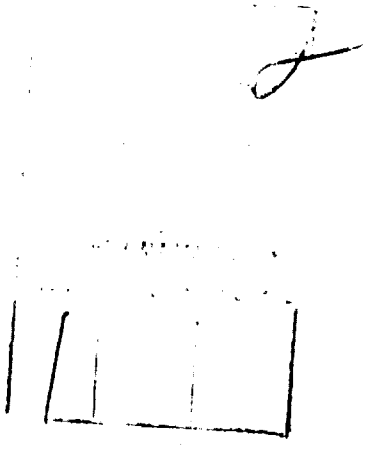

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FOREWORD

This report was prepared by the Ramjet Components Branch, Ramjet Engine Division of the Air Force Aero Propulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. The work was conducted under Task 301201, "Special Ramjets" of Project 3012, "Ramjet Technology."

The information herein was presented as a thesis in partial fulfillment of the requirements for the degree Master of Science by The Ohio State University. This report was submitted by the author July 1966.

The author wishes to express his appreciation to Professor R. Edse of The Ohio State University for his guidance, advice, and many helpful suggestions during the course of the investigation, and to Dr. A. D. Snyder of the Monsanto Research Corporation for making up the gas mixture and supplying the design for the transducer shock mounting system.

This technical report has been reviewed and is approved.

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ABSTRACT

An investigation of the ignition delay of bydrogen-air mixtures near the second explosion limit at pressures of 15 and 30 psia was made in a shock tube. The shock tube calculations are discussed along with the problems encountered during the investigation.

Attempts to correlate the data were satisfactorily accomplished when the HO_2 recombination rate was assumed to be proportional to $T^{-0.4}$.

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ILLUSTRATIONS

SYMBOLS

a	speed of sound (ft/sec)
c	species concentration (mole/liter)
g	gravitational constant (32.174 ft^2/sec)
h	enthalpy (Btu/lb)
J	mechanical equivalent of heat (778 ft-lb/Btu)
k	reaction rate constant
$\mathcal{M}$	molecular weight
P	pressure (lb/ft^2)
R	universal gas constant (1.987 calories/gm-mole °K)
T	temperature
u	particle velocity (ft/sec)
W	shock velocity relative to gas into which it is moving (ft/sec)
x	species mole fraction
α	$(\gamma+1)/(\gamma-1)$
β	$(\gamma-1)/2\gamma$
γ	ratio of specific heats (C_p/C_v)
ρ	density (lb/ft^3)
τ	ignition delay (seconds)

SUBSCRIPTS

1	conditions before shock in driven tube
2	conditions behind incident shock in driven tube
3	conditions behind contact surface in driver gas
4	initial conditions in driver tube
5	conditions behind reflected shock in driven gas
7	conditions behind reflected shock in driver gas
M	refers to some third body

SECTION I

INTRODUCTION

The mechanism of the hydrogen-oxygen reaction has been studied for many decades. In spite of the simple overall reaction, the actual mechanism has been subject to controversy for a number of years. If a reaction scheme is known, along with the rate constants for these reactions, the composition and temperature of the hydrogen-oxygen mixture can be computed as the mixture reacts. Ignition delay can be defined in a number of ways, but the definition must be such that the delay is experimentally detectable in order to check the calculations. Two of the most prevalent definitions of ignition delay are: (1) that point in time when there is a sudden increase in the pressure of the mixture and (2) that point in time when there is a sudden increase in the concentration of OH.

Various methods of experimentally determining ignition delays have been used. The principal ones include well-stirred reactors, flowing systems, and shock tubes.

The well-stirred reactor is a closed vessel containing heated air into which hot hydrogen is introduced and rapidly mixed with the air. The pressure of the vessel is monitored for a sudden rise, which signifies the end of the ignition delay period. The two disadvantages of this method are that the mixing tends to obscure the results when ignition delays on the order of a few hundred microseconds are being considered, and the results tend to depend on the vessel size and wall coating.

In the second method, hydrogen is introduced into a flowing system of subsonic air at a temperature slightly below the ignition limit. A diverging section slows the air down and raises the temperature of the mixture above the ignition limit. The distance from the diverging section to where combustion occurs, or the combustion zone, is used to calculate the ignition delay. With this method, however, it is difficult to obtain a uniform mixture and we must assume that no reaction has occurred before the mixture enters the diverging section.

The third method has become popular with the advent of the shock tube. The hydrogen-air mixture contained in the driven section of the shock tube is heated rapidly to the correct temperature and pressure by a normal shock wave. The time interval elapsed from the instant of the passage of the shock wave to the moment when the OH radiation appears is measured. When measurements are made behind the incident shock, a diluent, usually argon, is added to the hydrogen-oxygen mixture to prevent the heat released by the reaction from forming a detonation wave behind the normal shock wave. Measurements behind the reflected shock wave are also affected by the tendency to form detonation waves, and measurements cannot be made if the reflected shock wave is not past the measuring station before the heat is released. In this study, ignition delays on the order of 80-100 microseconds were measured before the formation of detonation waves became a problem.

Shock tube studies of the ignition delay in mixtures of hydrogen-oxygen have given support to a postulated reaction scheme and indicate that the initiation reaction is

$$H_2 + O_2 \longrightarrow H_2\,O_2^* \longrightarrow 2OH$$

and not

$$H_2 \longrightarrow 2H$$

Although the reaction scheme does predict correct values of the ignition delay at temperatures above 1100-1200°K, it does not properly account for the occurrence of the second

explosion limit of the hydrogen-oxygen reaction. To account for this limit, it was postulated that the reaction

$$H + O_2 + M \longrightarrow HO_2 + M$$

leads to a termination of the chain. HO_2 has never been observed, however, so this assumption is not entirely satisfactory, although a paramagnetic resonance spectra for the HO_2 molecule was observed recently (Reference 1) and a rate constant for the above reaction was established.

With this additional reaction, analytical expressions for the ignition delays of hydrogen-oxygen mixtures have been derived (Reference 2). These results explain the long ignition delays as the second explosion limit is approached. Data in this regime are scarce; only recently a comprehensive study was made (Reference 3), but these observations do not seem to follow any general pattern as to pressure dependence and they differ from the values obtained by the analysis of Reference 2. Therefore, there is some doubt as to the accuracy of these data.

On the basis of this information, it was decided to study the ignition delay of hydrogen-air mixtures under carefully controlled conditions. Near the second explosion limit, the ignition delay time changes drastically with small changes in temperature; therefore, the absolute values of ignition delay cannot be determined accurately. The general trend, however, is expected to provide a check on the analysis of Reference 2.

The reflected shock technique was used in this investigation so that we would not have to dilute the hydrogen-air sample to prevent the formation of detonation waves behind the incident shock when the ignition delay was short. In addition, the test time behind the incident shock was not sufficient for the case when the ignition delays were long. The tailored interface mode of operation was also used since test times as long as 10,000 microseconds might be required. In the tailored interface mode, the driver gas composition is adjusted such that the reflected shock wave will pass through the contact surface without propagating any disturbance into the test gas.

SECTION II

SHOCK TUBE CALCULATIONS

Since accurate temperature measurements behind the reflected shock are not possible at present, one must usually calculate the temperature from the measured shock wave velocity and initial conditions. From Reference 4, the general basic equations for a normal shock wave are:

Continuity:

$$\rho_1 W = \rho_2 \left[W \pm (u_1 - u_2) \right] \tag{1}$$

Momentum:

$$P_1 + \frac{\rho_1}{g} W^2 = P_2 + \frac{\rho_2}{g} \left[W \pm (u_1 - u_2) \right]^2 \tag{2}$$

Energy:

$$h_1 + \frac{W^2}{2gJ} = h_2 + \frac{\left[W \pm (u_1 - u_2) \right]^2}{2gJ} \tag{3}$$

where the (+) sign refers to a right-traveling wave and the (-) sign refers to a left-traveling wave.

For the general case of a reacting gas or a gas with variable specific heats, these equations must be solved by an iteration procedure. The conditions behind the incident shock are obtained by combining Equations 1, 2, and 3.

$$\frac{P_2}{P_1} = 1 + \frac{2J (h_2 - h_1)}{(1 + \rho_1 / \rho_2)} \frac{\rho_1}{P_1} \tag{4}$$

One first specifies a value for T_2 and then assumes a value for P_2 (obtained from an ideal gas formula). From this value of P_2 and T_2, h_2 and ρ_2 can be calculated and a new value for P_2 calculated from Equation 4. This calculated value of P_2 then becomes the new assumed value of P_2 and the process is repeated until the assumed and calculated values of P_2 are the same. The shock wave velocity is then computed from

$$W = \sqrt{\frac{P_1}{\rho_1} \frac{(P_2 / P_1 - 1)}{(1 - \rho_1 / \rho_2)} g} \tag{5}$$

The particle velocity behind the incident shock is

$$u_2 - u_1 = \sqrt{\frac{P_1}{\rho_1} \left(\frac{P_2}{P_1} - 1 \right) \left(1 - \frac{\rho_1}{\rho_2} \right) g} \tag{6}$$

where u_1 is normally zero.

For the reflected shock, the process becomes a little more complicated since there are two equations upon which to iterate. These equations are

$$P_5 = P_2 + \left[h_5 - h_2 + \frac{\left(\frac{P_2 - P_1}{\rho_1}\right)\left(1 - \frac{\rho_1}{\rho_2}\right)}{2J} \right] \rho_2 \, J \tag{7}$$

$$T_5 = T_2 \left\{ 1 - \frac{\left[\frac{(P_2/P_1 - 1)(1 - \rho_1/\rho_2)}{(P_2/P_1)(\rho_1/\rho_2)}\right]}{P_5/P_2 - 1} \right\} \frac{P_5}{P_2} \frac{m_5}{m_2} \tag{8}$$

One first assumes a value for P_5 from ideal gas formula and calculates a value for T_5 from Equation 8 by assuming m_5 equals m_2. With this value of T_5 and P_5, m_5 can be calculated and a new value of T_5 computed. This is repeated until two successive T_5's are the same. A value for P_5 is then computed from Equation 7 and the entire process is repeated until two successive values of P_5 are the same. The reflected shock velocity is then found from

$$u_{rs} = u_2 - W = \frac{-u_2}{(1 - \rho_2/\rho_5)} \tag{9}$$

For the simplest case when operating in the reflected shock mode, the test time is normally interrupted by an expansion wave or shock generated when the reflected shock passes through the discontinuity (contact surface) between the driver and driven gases. This test time can be extended by operating the shock tube in the tailored mode, which can be accomplished by one of two methods. The first method is to heat the driver gas to the proper temperature, which limits operation to shock speeds greater than the tailoring shock Mach number of the unheated driver gas. The second method limits operation to shock speeds below that for the pure driver gas; this is accomplished by introducing a foreign gas into the driver gas, thus altering the molecular weight and ratio of the specific heats of the driver gas.

To calculate the conditions required for tailored operation, one first writes the equations of the difference in particle velocity across the reflected shock in the driver and driven gases:

$$u_5 - u_2 = \sqrt{P_2 (P_5/P_2 - 1)(1 - \rho_2/\rho_5)/\rho_2}$$

$$u_7 - u_3 = \sqrt{P_3 (P_7/P_3 - 1)(1 - \rho_3/\rho_7)/\rho_3}$$

Now $P_3 = P_2$, $u_2 = u_3$, and $u_5 = 0$. The conditions required for tailoring are that $P_7 = P_5$ and $u_7 = 0$.

One then arrives at the conditions required for tailoring as

$$\frac{1 - \rho_2/\rho_5}{\rho_2} = \frac{1 - \rho_3/\rho_7}{\rho_3} \tag{10}$$

which can be rewritten as

$$\frac{T_3}{T_2} = \frac{\left[P_5/P_2 - (m_2/m_5)(T_5/T_2)\right]}{\left[(P_5/P_2)(m_2/m_3) - (m_2/m_7)(T_7/T_3)\right]} \tag{11}$$

For the case of an ideal gas in the driver section, Equation 11 can be written as

$$\frac{T_3}{T_2} = \frac{\left[P_5/P_2 - (m_2/m_5)(T_5/T_2)\right]\left[1+\alpha_4 (P_5/P_2)\right]}{(m_2/m_4)(P_3/P_2)(P_5/P_2-1)(\alpha_4-1)} \tag{12}$$

Since the reduction of conditions in the driver gas is the result of a series of infinitesimal isentropic expansion waves, T_3 may also be written as

$$T_3 = T_4 \left[1 - \frac{\gamma_4 - 1}{2a_4} u_2\right]^2 \tag{13}$$

To calculate the driver gas composition required for tailoring at shock speeds below the tailoring shock speed for the pure driver gas, one assumes a composition for the driver gas and calculates T_3 from Equations 12 and 13. New compositions are assumed until T_3 from both equations agree.

The ideal driver pressure can be calculated from

$$\frac{P_4}{P_1} = \frac{P_2/P_1}{\left(1 - \frac{\gamma_4 - 1}{2a_4} u_2\right)^{1/\beta}} \tag{14}$$

For a given shock speed, Equation 14 yields only an approximation of the pressure ratio required to produce a shock of given strength since the boundary layer growth behind the shock wave attenuates the shock as it proceeds away from the diaphragm station.

Equations 4 through 14 were programmed for the IBM 7094 to calculate all the conditions in the H_2-air test gas for shock Mach numbers between 2.2 and 3.2; the calculations allowed for variable specific heats but no chemical reactions. Another program was also written to calculate the conditions behind the shock wave for air, allowing the gas to be in chemical and thermodynamic equilibrium but assuming no ionization, for use during initial firing and calibration of the shock tube.

Figures 1 and 2 show the reflected shock temperature and pressure and were used to determine the test conditions from the measured shock speed. For long delay times (greater than 2 milliseconds), tailored operation is required. Figure 3 was used to determine the amount of nitrogen that had to be added to the helium driver for tailored operation.

Figure 4 shows the required pressure ratio across the diaphragm to produce a shock of given strength. Experimental pressure ratios are given to indicate the degree of shock wave attenuation. Figure 5 shows the pressure behind the incident shock. The lowest allowable value of reflected shock pressure was used in these tests to produce an incident shock pressure that was great enough to trigger the electronic instrumentation.

Figure 6 indicates the temperature behind the incident shock, which determines the upper limit of shock speed that can be investigated, since T_2 must be low enough that no reactions of the H_2-air mixture occur behind the incident shock.

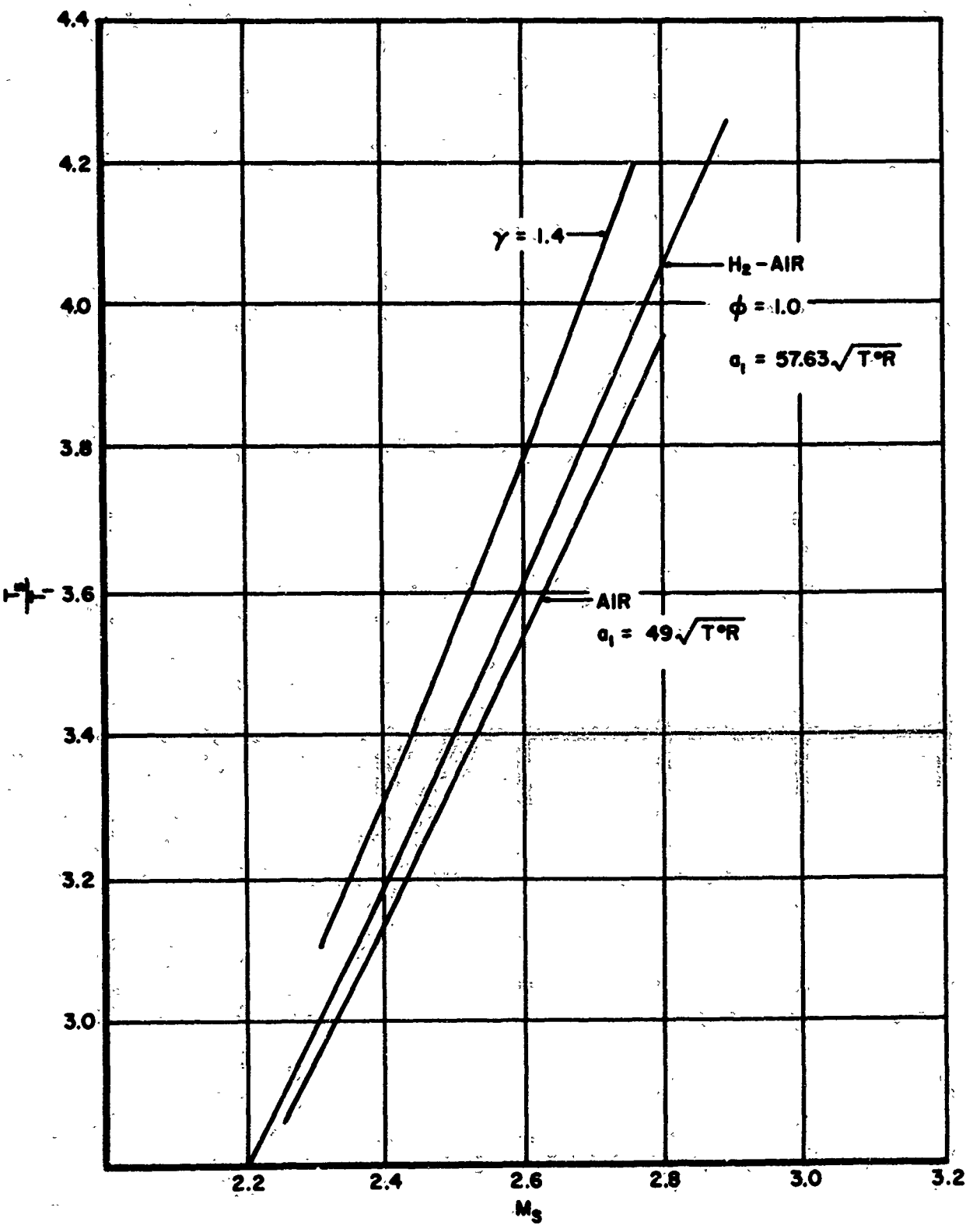


Figure 1. Reflected Shock Temperature Versus Shock Mach Number

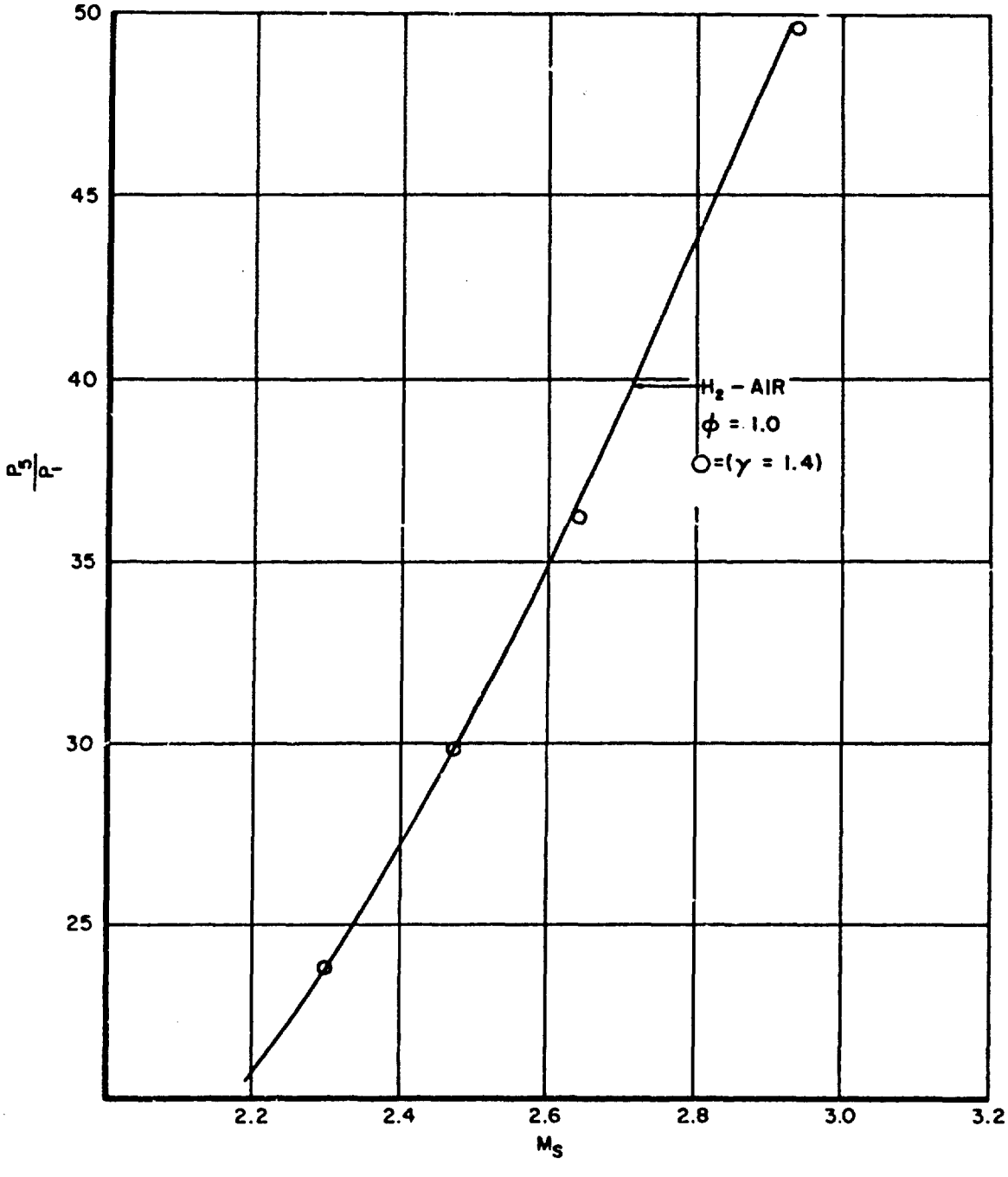


Figure 2. Reflected Shock Pressure Versus Shock Mach Number

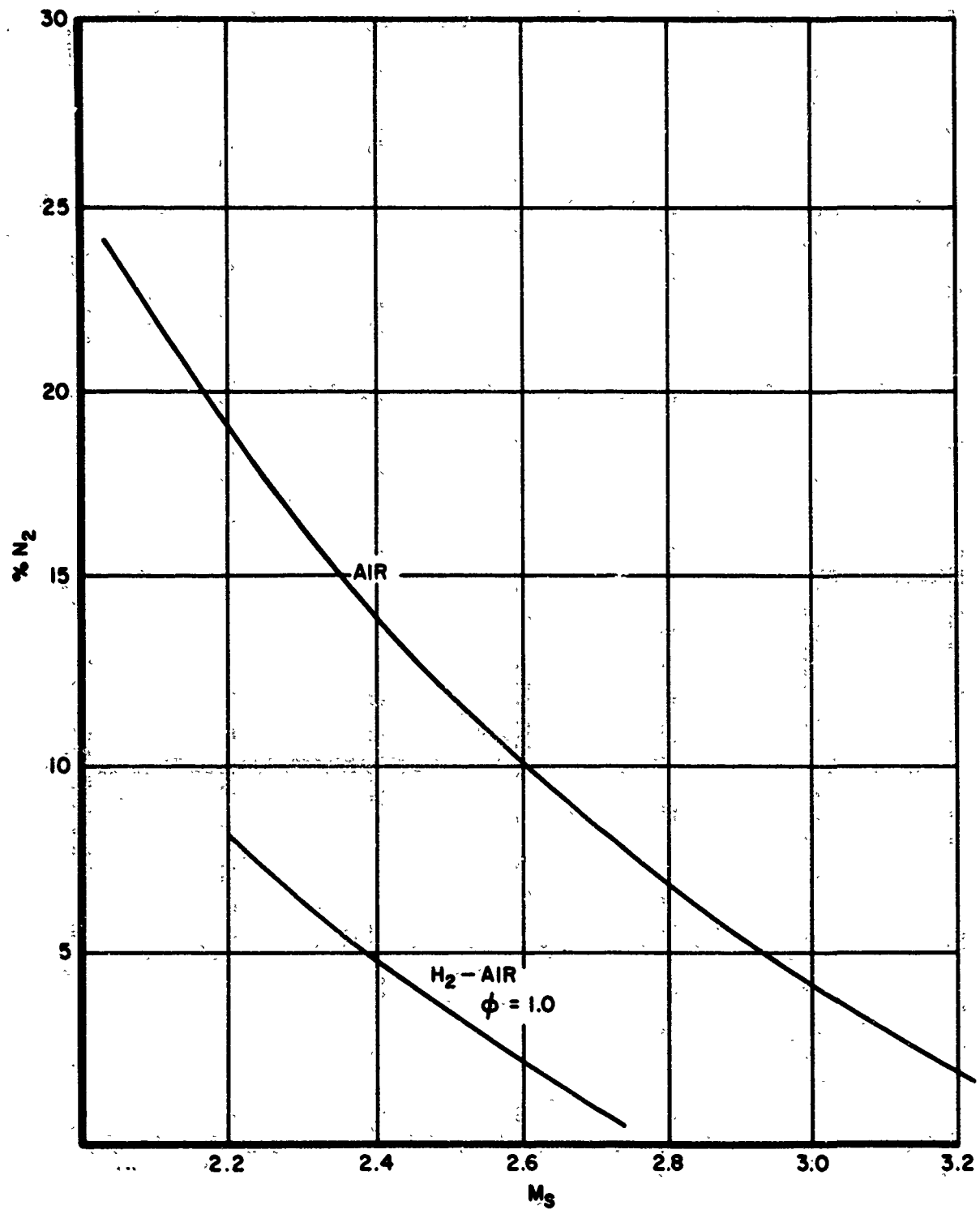


Figure 3. Percent N_2 Required for Tailoring With He-N_2 Driver Versus Shock Mach Number

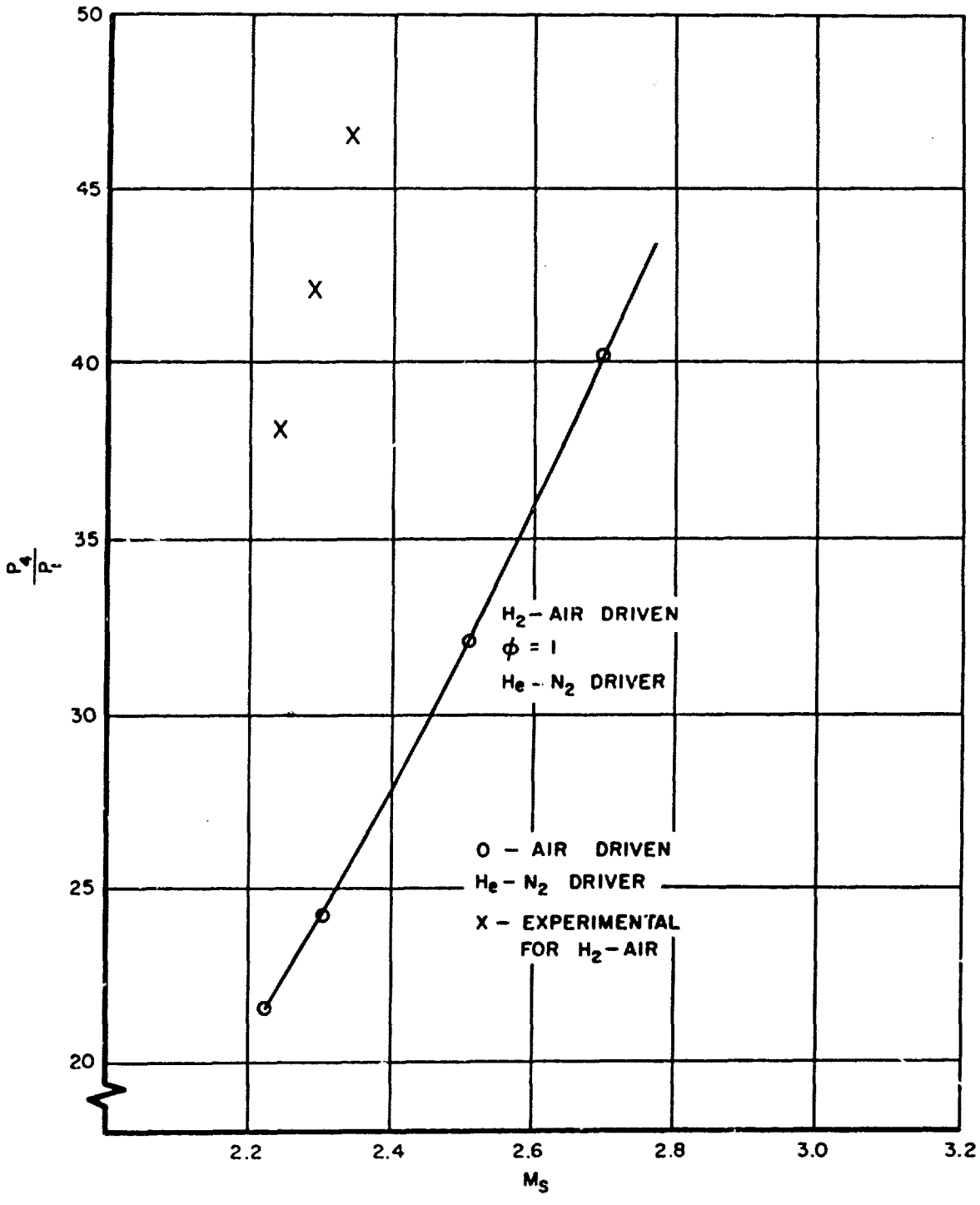


Figure 4. Diaphragm Pressure Ratio Versus Shock Mach Number

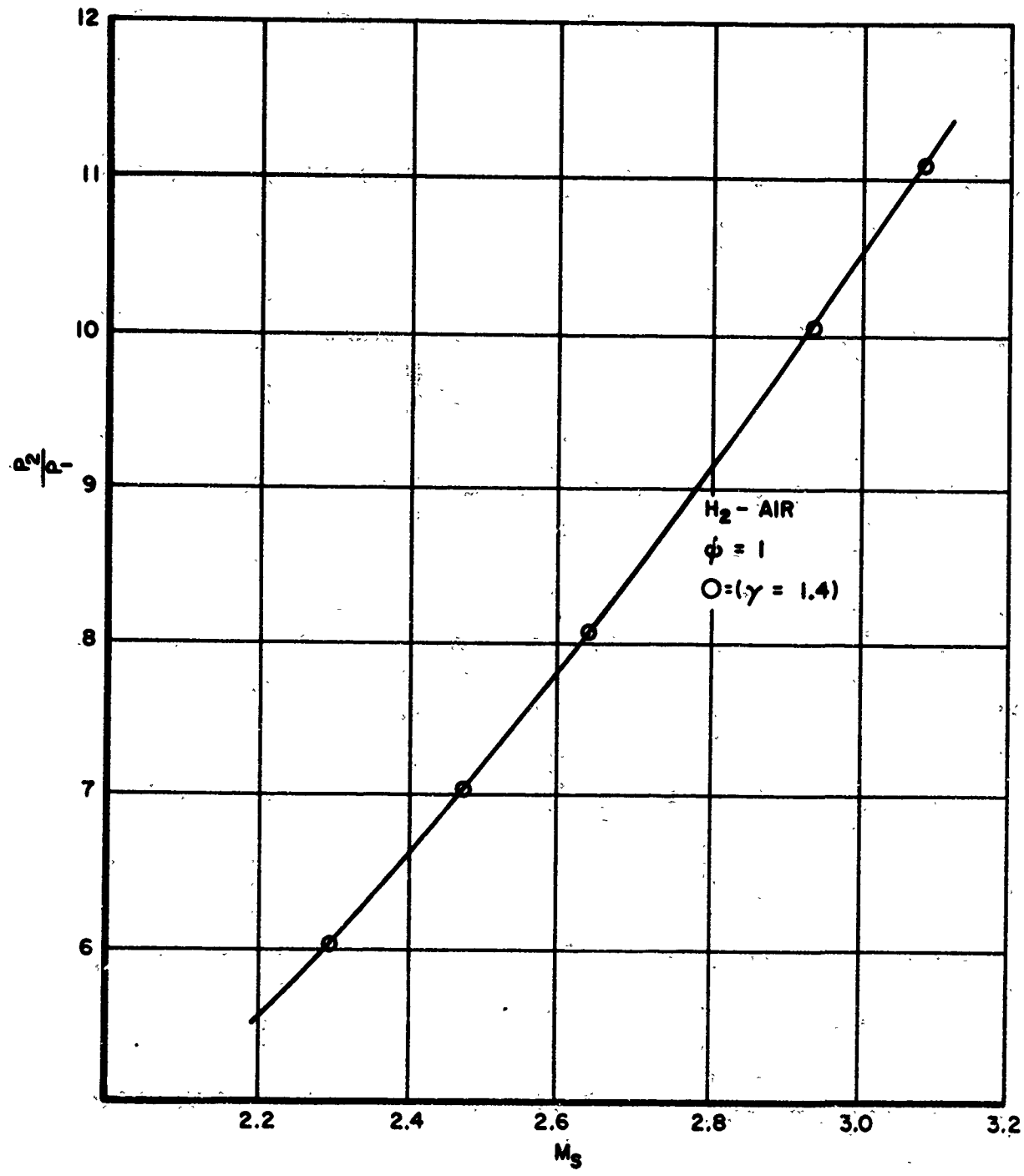


Figure 5. Incident Shock Pressure Versus Shock Mach Number

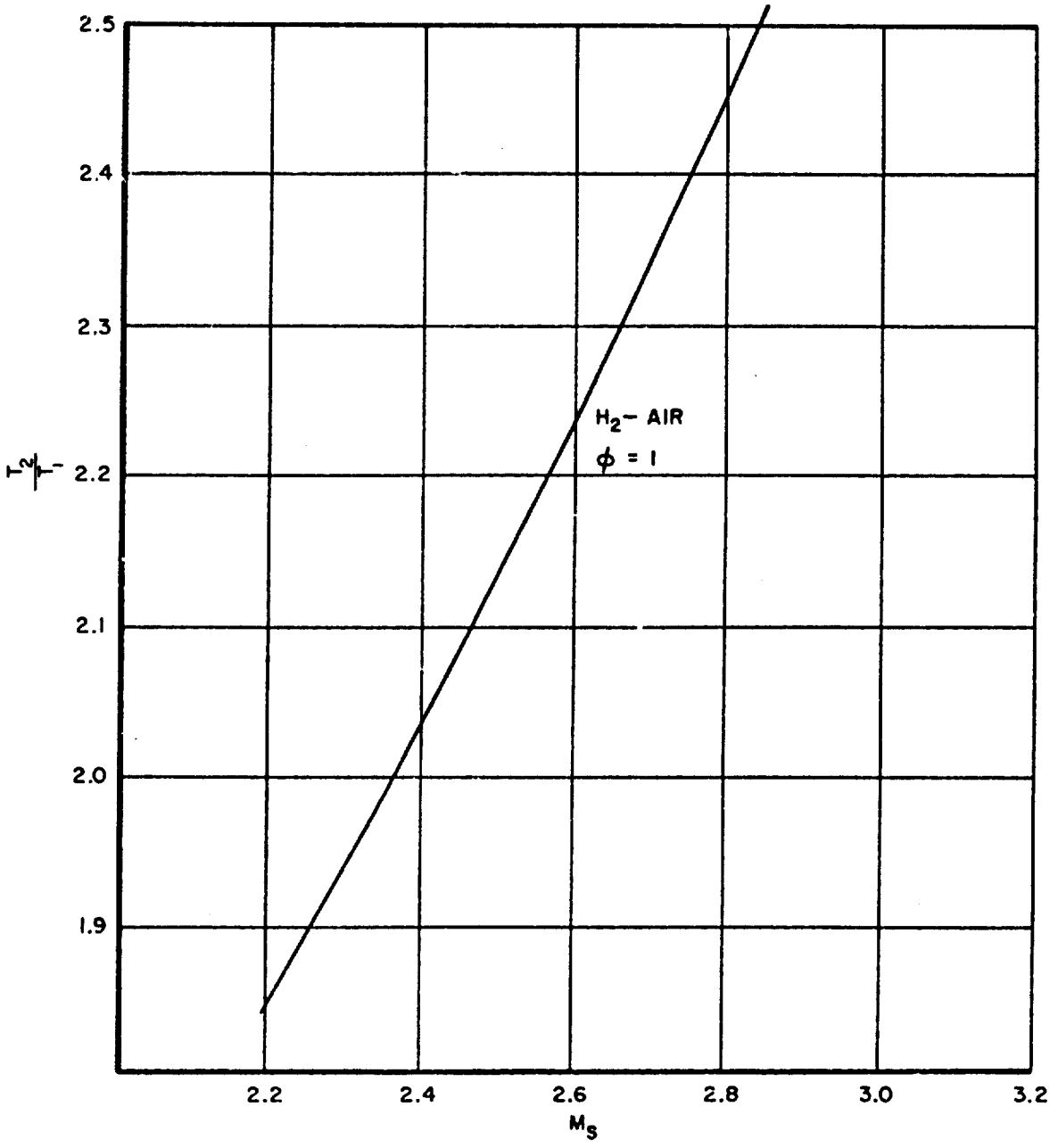


Figure 6. Incident Shock Temperature Versus Shock Mach Number

SECTION III

IGNITION DELAY COMPUTATIONS

In Reference 2 the following reactions were assumed to be of importance during the induction period:

$$OH + H_2 \xrightarrow{k_1} H_2O + H$$

$$H + O_2 \xrightarrow{k_2} OH + O$$

$$O + H_2 \xrightarrow{k_3} OH + H$$

$$H + O_2 + M \xrightarrow{k_6} HO_2 + M$$

$$HO_2 + H_2 \xrightarrow{k_{11}} H_2O_2 + H$$

where

$k_1 = 6.3 \times 10^{10}\ e^{-5900/RT}$ ℓ/mole-sec

$k_2 = 4.0 \times 10^{11}\ e^{-17{,}000/RT}$ ℓ/mole-sec

$k_3 = 1.2 \times 10^{11}\ e^{-8950/RT}$ ℓ/mole-sec

$k_6 = 3.27 \times 10^{15} (x_{H_2} + 0.35\, x_{O_2} + 0.43\, x_{N_2} + 0.2\, x_{A_r} + 14.3\, x_{H_2O} + ---)\, T^{-1.92}$ ℓ^2/mole^2-sec

$k_{11} = 5.4 \times 10^{8}\ e^{-24{,}000/RT}$ ℓ/mole-sec

The differential equations governing the growth of radical concentrations were then set up in Reference 2 for the induction period and a particular set of solutions were assumed, of the form

$$C_i = A_i\ e^{\lambda t} \qquad i = OH,\ H,\ O,\ HO_2$$

For the case of interest below the second explosion limit where $2k_2 > k_6\ C_M$

$$\lambda = \frac{k_1 k_3 (2k_2 + k_6 C_M) C_{H_2}^2 C_{O_2}}{k_1 k_3 C_{H_2}^2 + (k_1 + k_3) k_6 C_{H_2} C_{O_2} C_M + \left[(k_1 + k_3) C_{H_2} + (k_2 + k_6 C_M) C_{O_2}\right] \lambda + \lambda^2}$$

For the case where

$$k_6 C_M > 2k_2$$

$$\lambda \approx \frac{2k_2 k_{11} C_{H_2}}{k_6 C_M - 2k_2}$$

The end of the induction period was then defined to be when the concentration of OH reached 10^{-6} mole/liter, with the result

$$\tau = (B - \ell n P)/\lambda \qquad (15)$$

The value of the constant B was taken to be 25 to correlate high temperature ignition delay data where $2k_2 > k_6 C_M$. For longer delays where $k_6 C_M > 2k_2$, a value of B = 3.8 was found to correlate the experimental data. Equation 15 was then used to compute values for the ignition delay in the temperature range 1500-2000°R at pressures of 15 and 30 psia. The results are shown in Figure 7.

The theoretical analysis of molecular reaction rates of Reference 5, which has been used with good success in predicting reaction rates, indicates that recombination reactions, such as reaction 6, have rate constants proportional to $T^{-0.4}$. This temperature dependence has been experimentally undetectable due to inaccuracies in the experimental data, although it was believed that a temperature dependence should exist. The value of k_6 was then computed at 300°K from the equation of Reference 2. Using this value for k_6 at 300°K and assuming the rate to be proportional to $T^{-0.4}$, a new effective collision frequency was computed giving

$$k_6 = 6.24 \times 10^{10} \left(X_{H_2} + 0.35\, X_{O_2} + 0.43\, X_{N_2} + \text{---}\right) T^{-0.4}$$

With this new value for k_6, the ignition delay calculations were repeated. The results are shown in Figure 8.

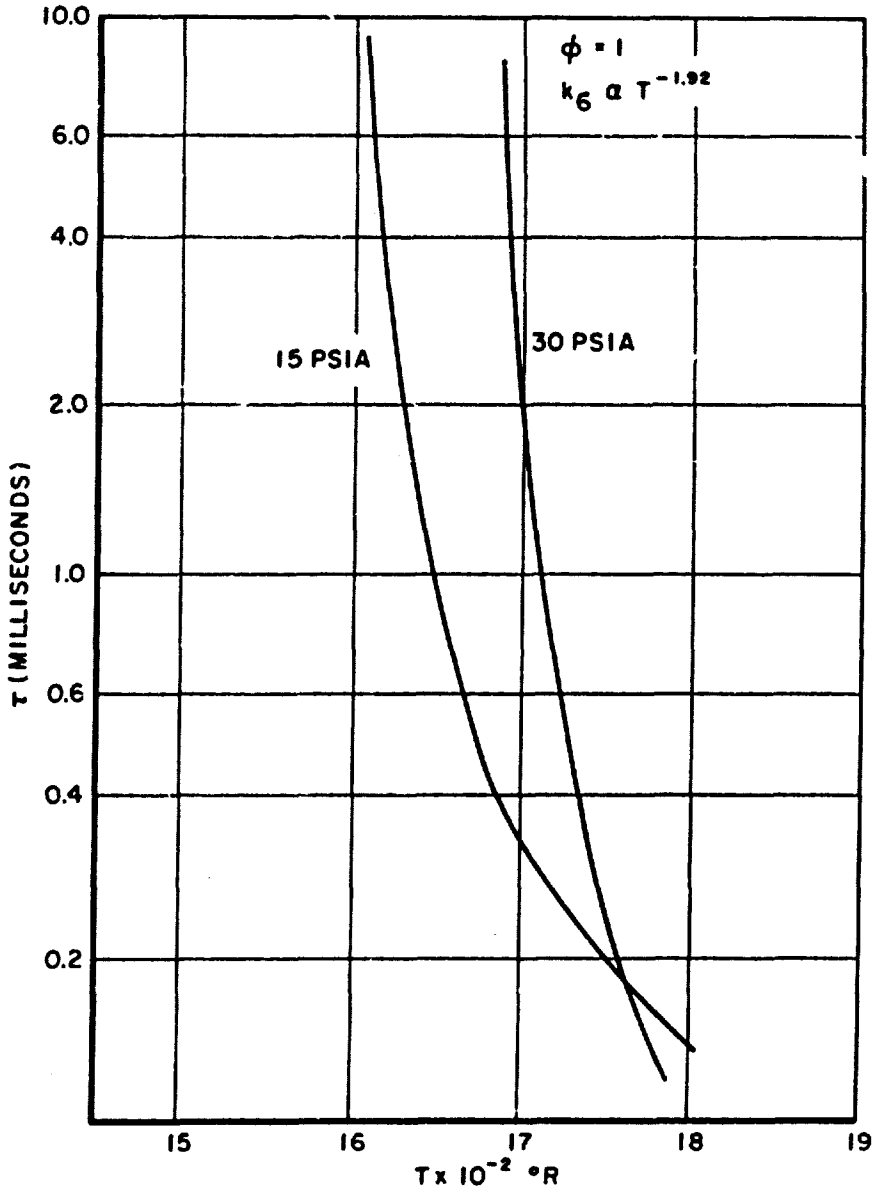


Figure 7. Ignition Delay of H_2-Air Versus Temperature

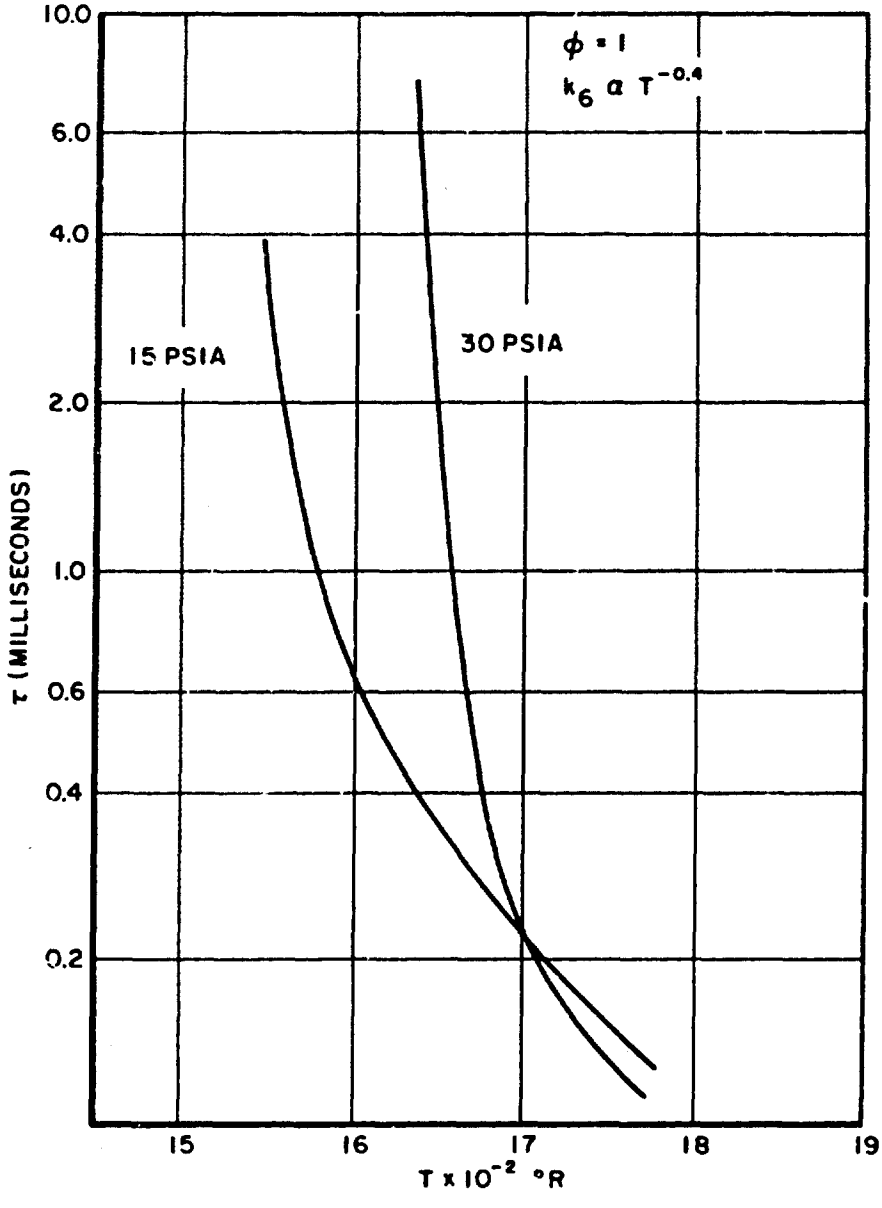


Figure 8. Ignition Delay of H_2-Air Versus Temperature

SECTION IV

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The shock tube used in this study consisted of a driver and a driven section, each constructed of 3-inch stainless steel pipe, 20 feet long, with no internal machining. Attached to the end of the driven section was a 2-foot test section containing a Kistler Model 603 quartz pressure transducer for monitoring the reflected shock pressure and two 1/2-inch-diameter quartz windows for monitoring the OH radiation during the combustion process. The quartz windows and pressure transducer were located 4 inches from the end of the test section. At a distance of 1.905 feet upstream, another pressure transducer was installed to trigger the electronic equipment. The time required for the shock wave to traverse the distance between the two pressure transducers was recorded on two Atec electronic counters.

The light output from the combustion process, initiated by the reflected shock, was passed through an Edmund's Scientific Company diffraction grating monochrometer set at 306 millimicrons. The light intensity from the monochrometer was then measured by an RCA photomultiplier tube. This data, together with the pressure measurements from the transducer, were recorded on three Tektronic 535 oscilloscopes.

The pressure transducers were mounted in the tube by means of a shock mounting system employing neoprene "O" rings to completely isolate the transducers from the tube. The mounting system was required to reduce the vibrations picked up by the transducers from the tube. The signals from the transducers were amplified by two Kistler 566 electrostatic charge amplifiers and recorded on the Tektronic oscilloscopes.

The double-diaphragm technique was used for rupturing the diaphragms. Two Mylar diaphragms of 0.001, 0.002, or 0.003 inch thickness, depending on the final pressure in the driver tube, were separated by a 1-inch metal plate. The driver section and the section between the diaphragms were loaded to one-half the final pressure. The driver was then pressurized to its predetermined final pressure, and the center section between the two diaphragms was vented to a vacuum tank, allowing the first diaphragm to be ruptured and then the second.

The hydrogen-air mixture was premixed in stoichiometric proportions in a clean gas bottle and filled to a pressure of about 100 psia. The mixture was introduced into the driven tube to the desired pressure after the tube had first been evacuated to about 200 microns. This pressure was measured with a Wallace and Tiernan 0-200 mm Hg absolute pressure gage.

For the tailored mode of operation, the nitrogen pressure in the driven tube was measured with a 0-200 inches of mercury Kollsman gage. The final driver pressure was recorded on a 0-100 psia Brown recorder.

SECTION V

DISCUSSION OF EXPERIMENTAL DIFFICULTIES

During the course of this investigation, many difficulties were encountered which made the evaluation of the measurements initially impossible.

The first of these difficulties was in obtaining proper triggering of the electronic instrumentation as the shock wave passed, which was necessary to make accurate shock speed measurements. This problem was at first attributed to high humidity since the room in which the experiments were being performed was not climate-controlled. Baking the transducers and cables did seem to help, but only temporarily. The co-axial cable between the transducers and charge-amplifiers was finally removed and the transducers were connected to the charge amplifiers with short lengths of Kistler low-noise cable. This change completely eliminated all difficulties in triggering and shock speed measurement.

The next problem was not as vital to the completion of the study as the first but was equally perplexing. As shown in Figure 9, all oscilloscope traces of the reflected shock pressure at tailored conditions exhibited a hump in the pressure trace approximately 2 milliseconds after the reflected shock passed. Although the pressure rise was only on the order of 10%, we needed to know whether this disturbance was caused by the specific shock tube being used in this investigation or if it was characteristic of all shock tubes. No mention of an equivalent problem was found in the literature. A great deal of effort, therefore, was expended in an attempt to eliminate this problem, but with no success. It was noticed after some time that the position of this hump varied noticeably with shock velocity, which, of necessity, implies that the disturbance is produced from the contact surface as the reflected shock wave passes. We concluded that a region of mixing exists at the contact surface between the driver and driven gases, such that, no matter what the shock speed, it is always overtailored. A series of weak compression waves and, subsequently, expansion waves are then produced as the reflected shock passes through this region. These conclusions were later confirmed by the results presented in Reference 6.

Another problem was encountered when the ignition delay experiments were started. The problem encountered at this point proved to be the most difficult of the entire experimental program. When the hydrogen-air mixture was introduced into the driven tube and the reflected shock was used to bring the temperature and pressure of the mixture up to a point where spontaneous combustion could occur, the mixture would ignite behind the incident shock, in a region where the temperature was only 700-800°R, which is well below the explosion limits for hydrogen-air. Observation of shock-heated air through the quartz windows showed the tube to contain burning particles. The tube was then completely disassembled and cleaned, but this did not change the behavior. Filters were placed on all gas lines entering the tube, but this did not solve the problem. Efforts to identify the nature of the particles were unsuccessful. A fine dust was noticed around the double diaphragm section of the shock tube, however, and when this dust was introduced around the quartz windows of the tube, a brilliant flash was observed at the window station when the tube was fired. We noticed that the arrangement of the double diaphragm section was such that small metal particles from the bars holding the double diaphragm were scraped off and entered the tube each time it was closed. The support bars were moved to the side of the tube, which seemed to end the problem and allowed the initial ignition delay data to be taken.

Over a period of several weeks, ignition delay data for reflected shock pressures of 15 and 30 psia and temperatures of 1580°R to 1800°R were obtained. A sample oscilloscope trace is shown in Figure 10 for P = 30 psia and T = 1705°R. The results of these experiments are tabulated in Table I and shown in Figures 11 and 12, along with the analytical predictions for

the two values of the rate constant k_6. Figure 13 shows how the data relates to the correlation of high-temperature data and emphasizes the fact that the high-temperature correlation cannot be used below temperatures of 1700 - 2000°R, depending upon the pressure of the mixture.

The temperatures for the data shown were calculated from the measured shock wave velocity. Several means of computing the temperatures were tried to see if the scatter in the data could be reduced, such as computing the temperature from the measured reflected shock pressure, and computing a temperature time history of the ignition period from the pressure trace and time averaging the curve to get an average temperature. Neither of these methods appeared to reduce the scatter of the data significantly.

The data, at first glance, appear to be quite scattered, but all but 8 of the 43 experimental points are within a ±2% temperature band of the analytical prediction for $k_6 \propto T^{-0.4}$. This would seem to lend support to the adoption of the reaction rate

$$k_6 = 6.24 \times 10^{10} \left(x_{H_2} + 0.35\ x_{O_2} + 0.43\, x_{N_2} + \text{---} \right) T^{-0.4}$$

This was a very limited amount of data on which to base such a conclusion, however, so additional experiments were planned. Since there is less slope to the computed ignition delay curve at low pressures, the obvious approach would be to use reflected shock pressures of 5 or 10 psia. The electronic counters required a signal of approximately 250 millivolts for reliable triggering and the pressure transducer output and amplifier gain produced only 39 millivolts per psi, however, so it was impossible to proceed with these lower shock pressures.

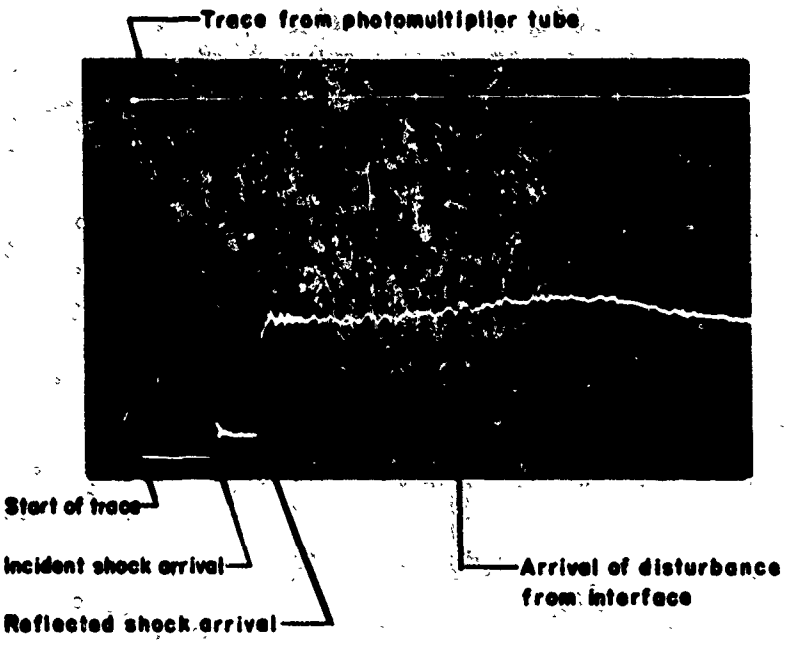
The next series of experiments was then planned to be conducted at 60 psia. In this set of experiments, the problem of ignition well below the ignition limits was again encountered, although the 15 and 30 psia data were still repeatable. Lowering the pressure to 45 psia provided no improvement nor did dismantling and cleaning the tube.

TABLE I

IGNITION DELAY OF H_2-AIR

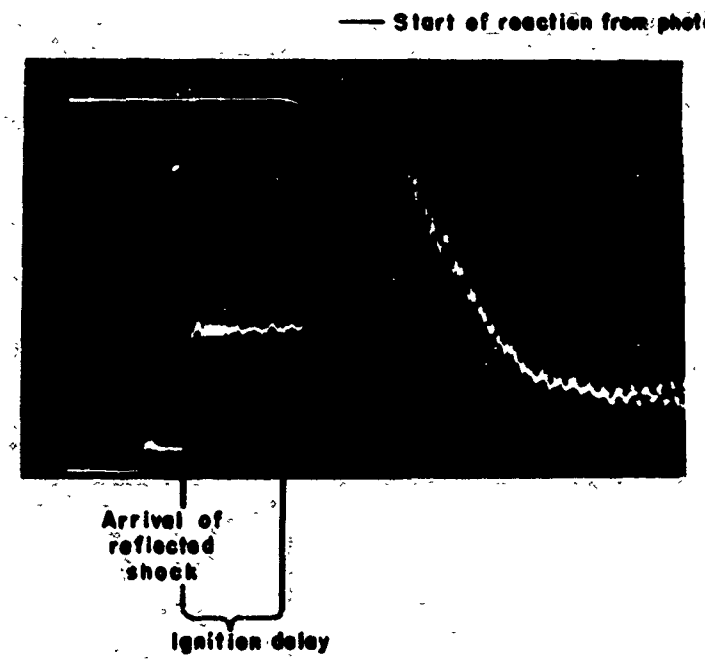
(ϕ =1)

15 psia		30 psia	
T (°R)	ms	T (°R)	ms
1575	3.25	1677	0.8
1655	0.3	1677	0.9
1655	0.3	1702	0.85
1580	0.595	1705	0.75
1648	0.51	1796	0.080
1690	0.41	1759	0.078
1682	0.41	1735	0.105
1710	0.225	1725	0.215
1725	0.27	1740	0.140
1710	0.25	1688	0.180
1767	0.11	1700	0.245
1704	0.355	1720	0.16
1735	0.205	1680	0.52
1600	0.7	1692	0.4
1582	1.85	1655	2.05
1591	1.6	1645	0.45
1775	0.12	1655	0.44
1575	2.4	1665	0.25
1631	0.48	1665	0.2
1580	1.25	1640	3.4
1596	1.5	1652	1.65
1595	1.35	1635	2.25



M_s = 2.20
P = 12.8 psi/cm
t = 0.5 ms/cm
T = 1603 °R
P_T = 28.6 psia

Figure 9. Oscilloscope Trace of Tailored H_2-Air With No Reaction



M_s = 2.42
P = 12.8 psi/cm
t = 0.5 ms/cm
T = 1705 °R
P_T = 28.4 psia
τ = 0.75 msec.

Figure 10. Oscilloscope Trace of H_2-Air With Reaction

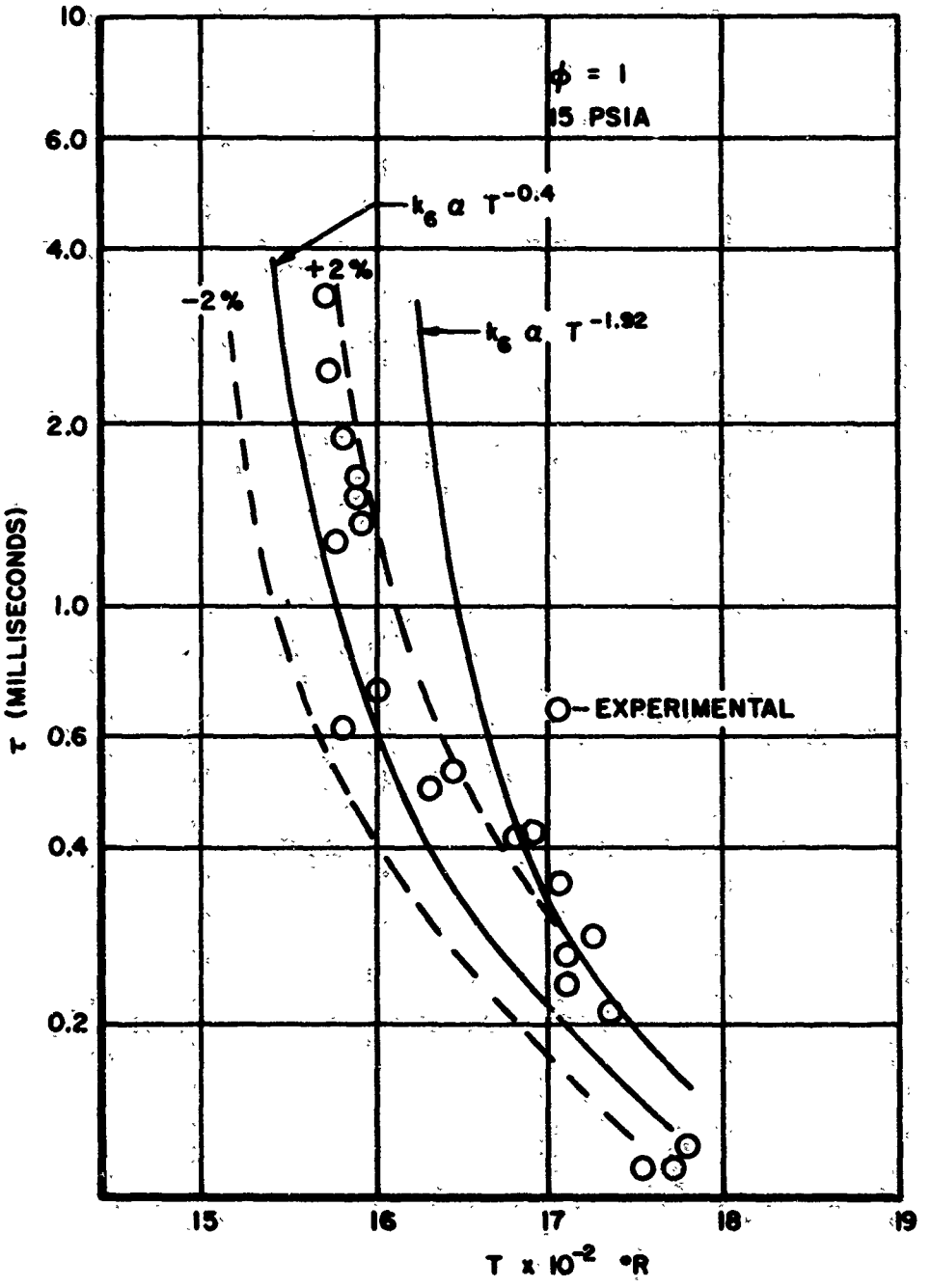


Figure 11. Ignition Delay of H_2-Air Versus Temperature, Shock Pressure of 15 psia

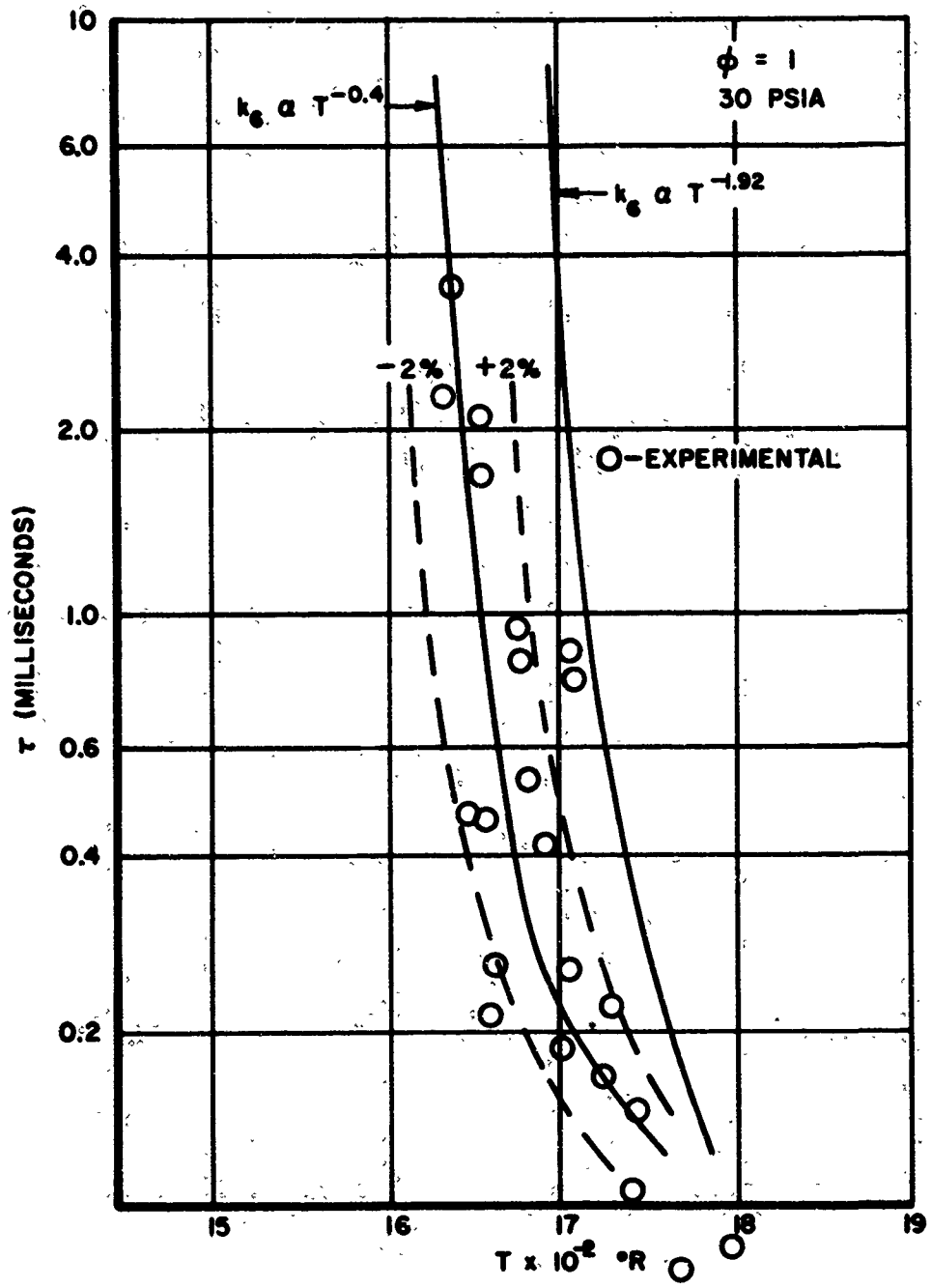


Figure 12. Ignition Delay of H_2-Air Versus Temperature, Shock Pressure of 30 psia

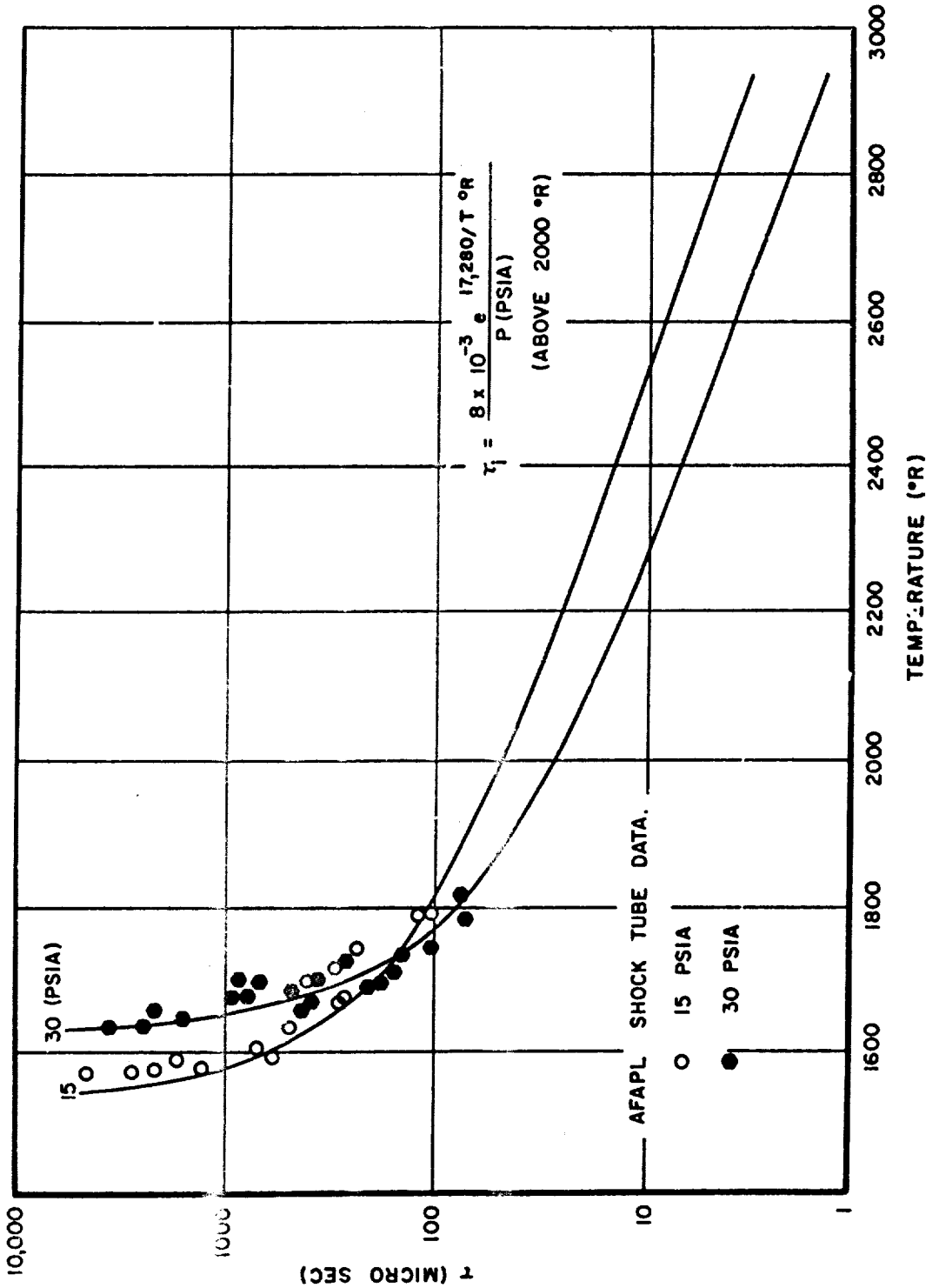


Figure 13. Ignition Delay of Stoichiometric H_2-Air Mixture Versus Temperature

SECTION VI

CONCLUSIONS

A shock tube was constructed and ignition delay data at 15 and 30 psia successfully obtained near the second explosion limit of hydrogen - air. Since the data were obtained for a stoichiometric mixture with no diluent, the data do not require extrapolation for use in air-breathing engine calculations. Also, the data emphasize the fallacy of extrapolating high temperature ignition delay data for hydrogen - air for use at conditions near the second explosion limit. In addition, the analytical technique of Reference 2, when applied with a modified reaction rate for the HO_2 recombination reaction, does predict the experimental results well within the accuracy of the data.

Many problems were brought to light and resolved, which should make further studies much less difficult and time consuming. A severe problem was encountered because the tube was constructed of stainless steel pipe of unknown origin, and there were many crevices in which foreign matter could accumulate. Future tubes will be constructed of new tubing which has been carefully reamed and cleaned, and which will have a minimum of instrumentation parts.

The results of this study suggest that additional work would be desirable in the following areas: (1) data obtained at higher and lower pressure than the present study to, hopefully, provide additional support for the recommended value of k_6 and (2) addition of various diluents to the hydrogen - air mixture to see if effect on the HO_2 reaction is as given in Reference 2. One other area to be investigated is the effect of catalysts on the ignition delay. It is known that the small amounts of NO_2 reduce the ignition delay at low temperatures by at least an order of magnitude; an investigation should be conducted to see if this effect is due to the NO released by the dissociation of the NO_2 and reacting with the H_2 or merely the atomic oxygen released by the dissociation of the NO_2. In addition, the use of a fine dust as an ignition source at very low temperatures should be investigated.

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13 ABSTRACT

An investigation of the ignition delay of hydrogen-air mixtures near the second explosion limit at pressures of 15 and 30 psia was made in a shock tube. The shock tube calculations are discussed along with the problems encountered during the investigation.

Attempts to correlate the data were satisfactorily accomplished when the HO_2 recombination rate was assumed to be proportional to $T^{-0.4}$.

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